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<b>(21) International Application Number:</b> PCT/US94/07168 <b>(22) International Filing Date:</b> 24 June 1994 (24.06.94)  <b>(30) Priority Data:</b> 08/239,085                      6 May 1994 (06.05.94)                      US  <b>(71) Applicant:</b> W.L. GORE & ASSOCIATES, INC. [US/US]; 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714 (US).  <b>(72) Inventors:</b> DUTTA, Anit; 5419 Pinehurst Drive, Wilmington, DE 19808 (US). HENN, Rober, Lyon; 2640 Longwood Drive, Wilmington, DE 19810 (US).  <b>(74) Agents:</b> SAMUELS, Gary, A. et al.; W.L. Gore & Associates, Inc., 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714 (US).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>  <b>BEST AVAILABLE COPY</b>
<b>(54) Title:</b> THREE-DIMENSIONAL SEAMLESS WATERPROOF BREATHABLE FLEXIBLE COMPOSITE ARTICLES  <b>(57) Abstract</b>  Waterproof, breathable, flexible, seamless shaped articles, such as gloves or socks, which are comprised of a flexible layered composite comprising: (a) a microporous thermoplastic polyester polyurethane or polyether polyurethane that is water vapor permeable, and (b) a hydrophilic nonporous copolymer that is waterproof but water vapor permeable which provides improved waterproofness to the microporous polymer layer.		

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**TITLE OF THE INVENTION**

THREE-DIMENSIONAL SEAMLESS WATERPROOF  
BREATHABLE FLEXIBLE COMPOSITE ARTICLES

**FIELD OF THE INVENTION**

5           This invention relates to three-dimensional, seamless, waterproof, breathable, flexible, composite articles for use in fabrics for clothing, such as gloves and stockings.

**BACKGROUND OF THE INVENTION**

10           Thin, breathable, form-fitting, articles such as gloves or socks are useful in many end uses, for example in medical, dental, or clean room applications.

          One convenient way of making such articles is to simply dip appropriately shaped formers into liquid elastomeric compositions so as to form a continuous film over the surface of the former.  
15           The film is then dried to form a solid film in the shape of the former. By choosing an elastomer that is liquid waterproof but breathable, a comfortable form-fitting glove can be easily prepared in one step. Preferably such gloves should be thin, e.g. 0.1 - 0.5 mm, and desirably easily stretchable.

20           One such class of elastomeric compositions into which formers can be dipped are those to form waterproof, breathable, microporous polyester or polyether polyurethane coatings, such as are described in USP 4,888,829. However, such microporous polyurethanes tend to lose some of their liquid waterproof nature when water pressure is applied against them. In addition, such microporous polyurethanes  
25           are susceptible to pore-clogging and contamination by sweat, etc.

          Another class of elastomeric composition into which formers can be dipped are solutions of hydrophilic polymers which when dried form a non-porous, liquid water impermeable but water vapor permeable film on the shape former. Typically, such non-porous  
30           films are stiffer than microporous films as evident from higher

modulus under tensile deformation. Since these unsupported non-porous films need to be of a certain minimum thickness for them to be useful as articles like gloves or socks, such articles are not very comfortable. Specifically, they are noisy and stiff, leading to poor fit and dexterity. It would be desirable to provide a film useful in form-fitting gloves, or useful in making a film for use in fabric structures that does not have the deficiencies recited above.

### SUMMARY OF THE INVENTION

This invention overcomes the deficiencies recited above by providing seamless shaped articles, such as gloves, socks or films, made of a flexible layered composite. One layer (I) of the composite is a microporous, elastomeric, thermoplastic polyester polyurethane or polyether polyurethane that is water vapor permeable. A second non-porous layer (II) is a hydrophilic nonporous continuous polymer that is waterproof but water vapor permeable and which improves the waterproofness of the composite over that of the microporous polyurethane layer (I) alone.

In one aspect the article is in the form of a glove. In another, it is in the form of a sock.

Preferably layer II will be 0.5 to 2 mils thick and layer I will be 5 to 50 mils thick.

By "hydrophilic" is meant that the material has a strong affinity for water and is capable of transporting water molecules through it. A convenient measure of affinity for water is the amount of water absorbed by the polymer under specified conditions. ASTM D570 is such a standard test method for determining water absorption of plastics. As used herein, hydrophilic is any polymer that shows greater than 5% (24 hour water absorption as per ASTM D570) water absorption by weight.

By "microporous" is meant that the layer has continuous pores from one side to the other that are very small.

By "breathable" is meant that the article has the ability to pass water vapor, such as in evaporated perspiration.

By "form-fitting" is meant that the gloves or socks, etc.,

will fit tightly around a hand or foot. The gloves should be thin and elastomeric in order to maintain good sensitivity for the wearer.

By "nonporous" is meant that there are no pores or passageways through the layer. One consequence is that the layer is not air permeable.

By "shaped article" is meant a form occupying a three-dimensional spacial configuration. As applied to garments it means a glove, hat or sock, rather than a planar film.

10

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a photomicrograph of the cross-section of the sample described in Example 1 at 400x magnification.

Figure 2 is a photomicrograph of the cross-section of the sample described in Example 4 at 200x magnification.

15 Figure 3 is a photomicrograph of the cross-section of the sample described in Comparative Example C-1 at 200x magnification.

Figure 4 is a photomicrograph of the cross-section of the sample described in Comparative Example C-5 at 60x magnification.

20 Figure 5 is a photomicrograph of the cross-section of the sample described in Comparative Example C-4 at 100x magnification.

Figure 6 is a photomicrograph of the cross-section of the sample described in Example 11 at 100x magnification.

Figure 7 is a photomicrograph of the cross-section of the sample described in Example 12 at 75x magnification.

25 Figure 8 is a photomicrograph of the cross-section of the sample described in Example 13 at 55x magnification.

### DETAILED DESCRIPTION OF THE INVENTION

#### Layer I - Polyurethanes

30 The microporous elastomeric, thermoplastic polyester polyurethanes or polyether polyurethanes used for layer I preferably have recovery properties intermediate between pure

rubbers and pure thermoplastic materials at room temperature.

The polyurethanes of layer I may be based on a wide variety of precursors which may be reacted with a wide variety of polyols and polyamines and polyisocyanates. As is well known the particular  
5 properties of the resulting polyurethanes to a large extent can be tailored by suitable choice of the reactants, reaction sequence and reaction conditions.

The preferred polyurethanes for layer I are elastomeric polyurethanes based on a linear, hydroxyl terminated polyester  
10 (although a polyether polyol or a polyether/polyester blend may be used) and a diisocyanate, with a small addition of a difunctional low molecular weight reactant. The last mentioned component may be added either with the other reactants at the start of a one-step polymerization or at a later stage when it will act primarily as a  
15 chain extender or partly at the start and partly later.

Particularly preferred polyurethanes for layer I are those derived from polyesters by reaction with diols and diisocyanates. As is known from United States Patent Specification No. 2,871,218 many different polyesters, diols and diisocyanates can be used, but  
20 a particularly suitable polyurethane system is one in which a polyester made from ethylene glycol and adipic acid is reacted with 1,4-butylene glycol and with 4,4'-diphenylmethane diisocyanate.

The mole ratio of polyester and diol can vary between quite wide limits but the combined number of moles of polyester and diol  
25 is arranged to be essentially equivalent to the number of moles of diisocyanate so that the resultant polymer is essentially free of unreacted hydroxyl or isocyanate groups.

The preferred polyurethane polymers for layer I are linear polyurethanes produced from a diisocyanate, a monomeric diol and a  
30 polyester polyol or a polyether polyol of molecular weight 1,000 to 3,000, the polyurethane having an intrinsic viscosity in dimethyl formamide of at least 0.5 dl/g.

Especially preferred polyurethanes for layer I may have a nitrogen content of about 3.0 to 4.0%, e.g. around 3.5%. Such  
35 material can be made by increasing the ratio of polyester to glycol resulting in a lower requirement of diisocyanate as compared to polyurethanes having a higher nitrogen content, such as 4.5% or more.

The polymers may be produced by a bulk polymerization process and subsequently dissolved in suitable solvents or may be prepared directly in solution by a solution polymerization process.

5 The polymer can include conventional stabilizers, fillers, processing aids, pigments, dyes, and additives such as surface active agents or proofing agents, and when the polymer content is quoted in the claims this includes any such additives which may replace up to 10% w/w of the polymer.

10 A further polyurethane system which has been found suitable for layer I uses polyesters derived from caprolactone. Such polyurethanes are described in British Patent Specification No. 859640.

#### Layer II - Nonporous Polymers

15 Turning now to the hydrophilic polymer component of layer II, it should have 24 hour water absorption value greater than 5% when tested as per ASTM D570.

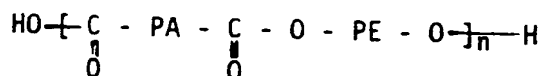
20 Layer II can be formed from such materials disclosed in USP 4,194,041, the disclosure of which is incorporated herein by reference; and from hydrophilic elastomers including but not limited to elastomers made from poly(esters), poly(amides), cellulose derivatives, poly(acrylic acid) and its homologs, natural or synthetic rubber with hydrophilic impurities, copolyoxamides, polyureas, polyelectrolytes, poly(phosphates), poly(vinylamine), poly(vinylalcohol), poly(ether) and copolymers thereof,

25 poly(thioether), polythioether-polyether, copoly(epichlorohydrinether), poly(sulphosphates), copolyester-ether and derivatives or mixtures thereof. Preferably, the hydrophilic polymer is a copolyetherester, polyurethane or a copolyetheresteramide. All these polymers are permeable to water vapor, but are highly impervious to liquid water.

30

A preferred class is hydrophilic copolyether esteramide. These polymers are a part of the general family of polyether block amide polymer chemistry as discussed in "Thermoplastic Elastomers - A Comprehensive Review" edited by N.R. Legge, G. Holden and H.E. Schroeder. The general formula of these copolymers is:

35



where PA is the polyamide block and PE is the polyether block. The development of these resins is described in U.S. Patent 4,230,838 which also discusses the potential for formulating hydrophilic grades using poly(alkylene oxide) glycol for the polyester block. A typical example of such a resin is PEBA<sup>®</sup> MX1074 available from Elf Atochem North America, Inc. The 24 hour water absorption capacity of this particular polymer is about 48% when tested as per ASTM D570.

The preferred hydrophilic copolyetherester polymers are segmented copolyesters that contain recurring long chain ester units of a dicarboxylic acid and a long chain glycol, and also contains recurring short chain ester units of a dicarboxylic acid and a short chain glycol. The glycol can contain ether units, in which case the copolyester is sometimes referred to as a copolyetherester. Hydrophilic copolyetherester compositions may be found in the teachings of U.S. Patent 4,493,870 and U.S. Patent 4,725,481 to Ostapchenko. A typical example of hydrophilic copolyetherester is Hytrel<sup>®</sup> HTR 8171 available from E. I. DuPont de Nemours and Co. The 24 hour water absorption capacity of this particular polymer is about 61% when tested as per ASTM D570.

The preferred hydrophilic polyurethane polymers are segmented block copolymers having a high concentration of oxyethylene units to impart hydrophilicity. Suitable compositions of such hydrophilic polyurethanes may be found by way of example in the teachings of U.S. Patent 4,194,041 to Gore and U.S. Patent 4,532,316 to Henn as also in publications like that on page 1419 of volume 47 of Journal of Applied Polymer Science by N.S. Schneider, J.L. Illinger and F.E. Kanasz. Hydrophilic polyurethanes are commercially available in various forms -- as solid resins, as reactive prepolymers and as solutions in organic solvent or solvent mixtures.

### 35 Preparation-Shaped Articles.

The invention also relates to methods of making the composites. In one method a seamless, waterproof, breathable and



composites. In one method a seamless, waterproof, breathable and form fitting article of the invention can be made by dipping a non-porous shape former into a bath containing a solution of the hydrophilic polymer (Layer II) and withdrawing it from the solution at a controlled rate to obtain a desired distribution of the solution over its surface. Solvent is then removed, for example, by drying, from the coated former to form a thin solid film of the hydrophilic polymer on top of the former. If the polymer is reactive, as in case of polyurethane prepolymers, the film is cured to complete the process of non-porous film formation. Examples of such curing process may be by reaction with ambient moisture, by heating to unblock any curing agents mixed into the prepolymer or by subjecting it to various forms of radiation to initiate and propagate the curing reaction.

The former with the non-porous hydrophilic coating, Layer II, on it is then dipped into a solution of a thermoplastic polyurethane Layer I composition in polar solvents such as dimethyl formamide (DMF), dimethyl acetamide, dimethyl sulfoxide, N-methyl pyrrolidone or the like, that are miscible with the non-solvent used, and withdrawing it from the solution at a controlled rate. The coated former is then manipulated to obtain a desired distribution of the solution over its surface. The coated former is then immersed in a bath containing non-solvent or solvent/non-solvent mixture (or mixtures) in order to convert the polyurethane coating into a microporous water vapor permeable coating. Some typical examples of the non-solvent are water and alcohol like methanol, ethanol, isopropyl alcohol. Water, however, is preferred due to environmental concerns and its ease of handling. The shaped composite article thus formed is then dried under ambient conditions or in an oven either after or before removing it from the shape former.

An added benefit of this composite construction is that due to the swelling of the hydrophilic polymer layer II, the shaped articles are relatively easily stripped from the former when the article is wet as compared to that when it is dry.

Alternatively, the former can be dipped first into a solution of the thermoplastic polyurethane for layer I in order to form the microporous layer. Once that is completed, the hydrophilic polymer

layer can be formed. Preferably, the former will be in the shape of a hand or a foot.

In another variation, the hydrophilic polymer Layer II can be sandwiched between two microporous polyurethane layers.

5     Conversely, the microporous polyurethane Layer I can be sandwiched between two layers of the hydrophilic polymer.

10     The above composite articles can also be provided with increased strength by forming the composite coating on a fabric, such as woven or non-woven shaped fabric liners that may or may not be stretchable. The hand or drape of the finished article can be controlled by controlling the depth of penetration by the coating liquids into the fabric liner. This can be done by altering the surface characteristics of the fabric liner by treating it with water repelling agents such that the coating liquid(s) does not  
15     instantaneously wet the liner. The time interval between coating deposition and beginning of coagulation can therefore be used to control the degree of penetration. Once the fabric liner is treated appropriately, the composite coating can be formed in several ways. For example:

20     (i) forming the nonporous polymer layer on the treated fabric liner and forming the microporous polyurethane layer on top of it.

25     (ii) forming the microporous polyurethane layer on top of the treated fabric and then forming the nonporous polymer layer on top of the microporous film.

   (iii) by sandwiching the nonporous polymer layer between two layers of microporous polyurethane layers.

#### Examples of Preparation of Seamless Shaped Articles

##### SOLUTION A:

30     A solution of a hydrophilic nonporous copolyetherester elastomer was prepared as follows:

   In a 10 gallon Versamix (Charles Ross & Son Co. NY) heated at 40°C, 19000 grams of 1,1,2-trichloroethane was charged along with 2200 grams of a hydrophilic copolyetherester elastomer (Hytrel® HTR  
35     8171). The entire mass was stirred for 3 hours in order to obtain

a clear solution. The solution was then discharged and stored at room temperature.

#### SOLUTION B:

5 A solution of a thermoplastic polyester polyurethane was made as follows:

10 In the 10 gallon Versamix heated at 40°C, 12200 grams of N,N-dimethylformamide (DMF) and 3100 grams of a thermoplastic polyester polyurethane TPU1 (weight average molecular weight of about 25000, specific gravity of 1.18, 24 hour water absorption of 1-2%) made by reacting MDI (diphenyl methane diisocyanate) with polycaprolactone diol and using butane diol as the chain extender) were charged. The entire mass was then stirred in the mixer for 4 hours under nitrogen in order to obtain a clear solution. The solution was discharged from the mixer into a plastic container and allowed to cool under ambient conditions.

15 13527 grams of the above solution was again charged into the above mixer along with a mixture of 458 cc of distilled water and 67.5 grams of nonionic surfactant (FLUORAD®, FC-430 from 3M). The entire mass was stirred for 1 hour at ambient temperature to obtain a clear solution. The solution was then discharged from the mixer and stored under ambient conditions.

#### Example 1

25 A non-porous ceramic handform (glazed finish from General Porcelain Co., New Jersey) was dipped (fingers first) into Hytrel SOLUTION A. The form was then withdrawn at a controlled speed, and allowed to drain for 3 minutes with the finger pointing downwards. After this, the form was inverted and allowed to drain for 60 seconds with the fingers pointing upwards. The form was reinverted and allowed to air dry with the fingers pointing downwards.

30 The form, so coated, was dipped in polyurethane SOLUTION B. The form was then withdrawn at a controlled speed, allowed to drain for 1 minute with fingers pointing down, then the form was inverted and allowed to drain for 30 seconds with the fingers pointing up and finally the form was immersed in a 50/50 DMF/water (Dimethyl

formamide) mixture with fingers pointing down. After 15 minutes in the DMF/water mixture, the form was withdrawn and then immersed in water for 45 minutes after which the form was withdrawn and allowed to air dry. The glove shaped article was easily stripped from the former by injecting water between the glove and the former. The glove was destructively tested for various properties in the palm and the back of the palm area and the results are listed in Table 1.

#### Example 2

The same procedure was used as in Example 1 except, after dipping in SOLUTION B, the immersion times were 15 and 75 minutes in 50/50 DMF/water and in water respectively.

#### Example 3

The same procedure was used as in Example 1 except a ceramic handform with a bisque finish (from General Porcelain Co.) was used and, after dipping in SOLUTION B, the immersion times were 5 and 45 minutes in 50/50 DMF/water and in water respectively.

#### Example 4

The same procedure was used as in Example 3 except that, during step 2, after dipping in SOLUTION B, the coated handform was immersed only in water for 60 minutes.

#### Comparative Example C-1

The same procedure was used as in Example 1 except that the form was not dipped into SOLUTION A. It was dipped into polyurethane SOLUTION B only. Moreover, a handform with a bisque finish was used. As a result the glove formed has no hydrophilic

nonporous polymer film layer. During stripping from the handform, the glove tore in the finger crotch areas.

### Comparative Example C-2

A ceramic handform with a glazed finish was dipped (fingers first) in SOLUTION B, withdrawn at a controlled speed and drained for 1 minute with the fingers pointing down. The form was then inverted and drained for 20 seconds with the fingers pointing up. The form was then reinverted and immersed in water for 90 minutes after which it is withdrawn and air dried. Thus the glove has no hydrophilic nonporous polymer layer. The dried glove was then stripped off from the handform. The stripped glove was weak and tore in the finger crotch area during the process of stripping.

TABLE 1

EXAMPLE

	1	2	3	4	C-1	C-2
<u>Samples from Back of the Palm Area</u>						
Thickness <sup>1</sup>	7.80	7.20	8.36	12.3	9.30	3.40
MVTR <sup>2</sup>	1502	1418	1109	1081	1902	7327
Suter Test <sup>4</sup>	P3	P3	P3	P3	F1	F1
Water Entry Pressure <sup>3</sup>	119	123	114	108	----very low*----	
Stress at 100% strain <sup>5</sup>	289	288	258	180	114	176
Stress at Break <sup>5</sup>	797	823	713	351	311	578
Elongation at Break <sup>5</sup>	539	545	551	418	472	483
Tear Propagation <sup>6</sup>	48.5	51.9	49.8	58.3	33.0	35.0
<u>Samples From the Palm Area</u>						
MVTR <sup>2</sup>	1996	1707	1222	1222	1215	4123
Suter Test <sup>3</sup>	P3	P3	P3	P3	F1	P2
Water Entry Pressure <sup>4</sup>	120	124	110	120	----very low*----	

<sup>1</sup> as described under "THICKNESS" in U.S. Patent 5,036,551 to Dailey. Units are in mils.

<sup>2</sup> as described under "WATER VAPOR TRANSMISSION RATE" in U.S. Patent 5,036,551 to Dailey. Units are in gm./sq.m./day.

<sup>3</sup> as per Federal Test Method Standard No. 191A, Method 5512. Units are in psi. A taffeta fabric restraint conforming to type III, Class I restraint of MIL-C-21852 was used.

<sup>4</sup> as per Federal Test Method Standard No. 191A, Method 5516. The first letter F or P respectively indicate if the sample did or did not leak water. The second digit indicates the pressure in psi at which this happened.

<sup>5</sup> as per ASTM D882-83. Units for stress are in psi.

<sup>6</sup> as per ASTM D1938. Units are maximum load per inch of sample thickness.

\*cannot detect precisely, anywhere between 1 to 5 psi.

Example 5

The same procedure was used as in Example 1 except that a ceramic handform with bisque finish was used. The glove was tested for MVTR and the values were 1186 in the palm area. The  
5 waterproofness of the glove was then checked as per the "liquid water leakage" test procedure provided in U.S. Patent 5,036,551. The glove received a pass rating.

Figures 1, 2 and 3 show the cross-sectional SEM micrographs of the samples described in Examples 1, 4 and C-1 respectively.

10 Example 6

## SOLUTION C:

In a 10 gallon Versamix heated at 45°C, 17759 grams of Solution A was charged along with 3541 grams of 1,1,2-trichloroethane. The entire mass was stirred for 1 hour. The  
15 clear solution was then discharged and stored at room temperature for later use.

## SOLUTION D:

A solution was first prepared by mixing 3550 grams of a thermoplastic polyester polyurethane TPU2 (Texin® 480A from Miles  
20 Inc., weight average molecular weight = 133000, specific gravity = 1.20 and 24 hour water absorption of 1.5%) with 19310 grams of DMF for 5 hours in a 10 gallon Versamix at 40°C. The solution was then discharged and stored under ambient conditions for further processing. 20517 grams of this solution was recharged into the  
25 Versamix at 50°C and a preblended mixture of 100 grams of a surfactant (Fluorad® FC-430), 721 grams of distilled water and 110 grams of a defoamer (BYK®-066 from BYK Chemie) was added. The entire mass was mixed for 150 minutes to obtain a clear homogeneous liquid. This liquid was then discharged and stored under ambient  
30 conditions.

A non-porous handform (bisque finish) was dipped (fingers first) into SOLUTION C. After 10 seconds, the form was then withdrawn at a controlled speed, drained of excess liquid for 60

seconds. After that, the form was gently rotated and inverted to allow the draining of the liquid to occur for 150 seconds with the fingers pointing upwards. The form was then reinverted, drained another 180 seconds with the fingers pointing downwards. The form was then allowed to dry completely in air with the fingers pointing up. Once the coating was dried, the entire procedure was repeated.

The handform, so coated, was dipped in polyurethane SOLUTION D. The form was then withdrawn at a controlled speed, allowed to drain for 1 minute with fingers pointing down, then the form was gently inverted and rotated and allowed to drain for 60 seconds with the fingers pointing up and finally the form was immersed in water with the fingers pointing down. After 60 minutes, the form was withdrawn, excess water was removed and then the coated form was dried in an oven at 80°C for 30 minutes. The dried form was then immersed in water and the glove was stripped from the form and air dried.

The glove was destructively tested for various properties by taking samples from the palm or the back of the palm area. The data are shown in Table 2.

#### 20 Comparative Example C-3

The same procedure as in Example 6 except that the form is not dipped into SOLUTION C. It was dipped into polyurethane SOLUTION D only. During stripping from the handform, the glove tore in the finger crotch areas.

Table 2

	Example 6	Comparative Example C-3	
	Thickness <sup>1</sup>	9.63	12.58
	MVTR <sup>2</sup>	713	1996
5	Suter Test <sup>4</sup>	P3	F1
	Water Entry Pressure <sup>3</sup>	173	6
	Stress at 100% Strain <sup>5</sup>	686	82
	Stress at Break <sup>5</sup>	1677	403
	Elongation at Break <sup>5</sup>	313	383
10	Tear Propagation <sup>6</sup>	62.7	23.5

Example 7

15 The same procedure as in Example 6 except that the handform was dipped in SOLUTION C only once to form a thinner hydrophilic coating. The waterproofness of the glove was then checked as in Example 5. The glove received a pass rating. In the palm area, the MVTR was 1223 and Suter test indicated no leakage at 3 psi water pressure.

Example 8

20 A hydrophilic polyoxyethylene polyether polyurethane made according to teachings of U.S. Patent 4,532,316 and U.S. Patent 5,036,551 was used in this example. When a moisture cured film of this hydrophilic polyurethane was tested as per ASTM D570, the 24 hour water absorption was 132%.



## SOLUTION E:

A solution was prepared by dissolving about 100 grams of this hydrophilic, reactive polyurethane in mixture of 225 grams of tetrahydrofuran (THF) and 75 grams of DMF. Stirring, at room temperature was necessary to obtain a clear solution.

A clean 300 ml. glass beaker was manually dipped in SOLUTION E, gently withdrawn from it and allowed to dry as well cure for 24 hours by reacting with the ambient moisture.

The coated glass beaker was then dipped manually in SOLUTION D, drained of the excess liquid and immersed in water for 60 minutes before drying it under ambient conditions. The dried shaped article was then stripped off the glass beaker and tested for leakage by filling it with water. No water leakage was noticed.

The article was then air dried, the bottom end was cut off to create a tube which was then split to create a flat film. In an area of the film where the thickness was about 30 mils, the MVTR was 879, the water entry pressure was 172 psi and the film showed no leakage even at 2.25 psi pressure in the Suter test. These results, when compared to those of comparative Example C-3, demonstrates the improved waterproofness of the present invention.

Example 9

## SOLUTION F:

A breathable polyurethane solution SOLUCOTE TOP 932 (solids 42% approximately) was obtained from Soluol Chemical Co. A film was cast from this solution on release paper using a 20 mil drawdown bar (BYK Gardner) and dried under ambient conditions. The dried film was then heated in an oven at 155°C for 5 minutes before peeling it off from the release paper. 24 hour water absorption of this film was 66%.

The SOLUCOTE TOP 932 solution was diluted by mixing 125 grams of it with 132 grams of toluene and 243 grams of DMF at room temperature. A clean 300 ml. glass beaker was manually dipped in

SOLUTION F, gently withdrawn from it and allowed to dry under ambient conditions to form a hazy film. The coated glass beaker was then heated in an oven at 155°C for 90 seconds.

5 The coated glass beaker was then dipped manually in SOLUTION D, drained of the excess liquid and immersed in water for 60 minutes before drying it under ambient conditions. The dried shaped article was then stripped off the glass beaker and air dried. The bottom end was then cut off to create a tube which was  
10 further split into a flat film. In an area of the film where the thickness was about 30-35 mils, the MVTR was 1483, the water entry pressure was 26 psi. These results indicate the improved waterproofness of the composite article over an article made from just microporous polyurethane as detailed in comparative Example C-3.

15 Example 10

A clean glass former in the shape of a large (about 3 inches diameter) test tube was dipped manually in SOLUTION F up to a height of about 5 inches, gently withdrawn and allowed to dry under ambient conditions to form a hazy film. The coated glass form was  
20 then heated in an oven at 155°C for 2 minutes. Subsequently, the coated glass form is manually dipped in SOLUTION D up to a height of about 5 inches, drained of the excess and immersed in water for 60 minutes before drying it in air under ambient conditions. The dried shaped article was then stripped off the glass form and  
25 filled with water. No water leakage was noticed. The article was then dried and split to allow further testing. In an area of the film where the thickness was about 25 mils, the MVTR was 1497, the water entry pressure was 14 psi and the film showed leakage only at 1.5 psi pressure in the Suter test. When compared with the results  
30 of the comparative article C-3, the present article is seen to have improved waterproofness.

EXAMPLES OF PREPARATION OF SEAMLESS SHAPED ARTICLES  
WITH FABRIC SUPPORT

These examples are directed to making seamless sock inserts by forming the above composite film reinforced with a fabric support.

- 5 The knitted fabric used was a Fashion Color Knee High (made of 100% nylon and distributed by American Stores Buying Company, Salt Lake City, UT 84130) treated with fluorochemical based water-repelling agents to impart an oil rating of 6 as per AATCC Method No. 118-1983. Before the treatment, the oil rating was less than 1 and it  
10 was readily wetted by water.

Example 11

- Step 1 - The treated knee high was slipped on a shoe last (men's size 10 from Sterling Last Co., New York) and stretched adequately to conform exactly to the shape of the last. The entire  
15 assembly was then dipped (toe first) into SOLUTION A, and drained with the toe pointing down for 3 minutes. The last was then inverted and drained with the toe pointing up for 60 seconds and then it was air dried with the toe pointing down.

- Step 2 - The above last, with the hydrophilic polymer coated  
20 fabric on it, was then dipped (toe first) into SOLUTION B, withdrawn and drained for 1 minute and immersed into water for 48 hours. The last was then taken out of the water and air dried. After drying, the composite coating was then stripped from the last to give a seamless shoe-shaped article which is soft and elastic.  
25 and can serve as a sock insert. The article was then tested for moisture vapor transmission and waterproofness. These are listed in Table 3.

- Once the above sock insert was put on a foot, it gave a snug fit and was very comfortable because of its breathability and the  
30 low forces required to flex the foot. The above sock insert was also tested for water leakage by filling it up with 500 cc of water and observing for any signs of leakage. No water leakage was observed.

Example 12

The same procedure was used as in Example 11 except that step 2 was conducted first with 16 hours of immersion in water. The dried microporous layer (on the treated fabric support) was then coated with a thin layer of hydrophilic polymer as in step 1 of Example 11. Similar observations as in Example 11 showed no water leakage when filled with water.

Comparative Example C-4

The same procedure was used as in Example 12 except that no hydrophilic coating was deposited on the microporous layer. This sample was even softer and more elastic than samples in Examples 11 and 12. Even though it was extremely form fitting and comfortable, it leaked through isolated coating defects (like pinholes) when filled with 500 cc of water and showed signs of water seepage through the microporous layer under slight pressure.

Comparative Example C-5

The same procedure was used as in Comparative Example C-4 except that the fabric support was not treated with water repelling agents. This sample was also form fitting, but on filling with water it showed signs of seepage.

TABLE 3EXAMPLES

		11	12	C-4	C-5	Base Fabric
<u>Samples From the Toe Area</u>						
	MVTR <sup>2</sup>	644	1215	1852	2155	5573
30	Suter Test <sup>4</sup>	F2	P3	F1	F1	---
<u>Samples From the Heel Area</u>						
	MVTR <sup>2</sup>	846	9111	2948	2539	5573
35	Suter Test <sup>4</sup>	F2	P3	F1	F1	---

Figures 4, 5, 6 and 7 show the cross-sectional SEM pictures of the samples described in Examples C-5, C-4, 11 and 12 respectively.

Example 13

5 A woven sock made of 93/7 cotton/Lycra® Spandex (women's style 9031 Charter Club from R.H. Macy and Co., Inc.) was treated with fluorochemicals to give an oil rating of #6. Before treatment, the oil rating of the sock was less than #1. The treated sock was then coated following steps 1 and 2 as described in Example 11 except that a smaller footform (women's size 6) was used. The footform  
10 was then taken out of the water and air dried. The coated sock was then stripped of the footform to give a seamless shaped article. Although stiffer than the original sock, the coated sock was elastic and soft enough to provide a snug and comfortable fit to the foot. The coated sock showed no sign of water leakage when it  
15 was filled with 500 cc of water and the MVTR in the area just above the ankle was 422.

Figure 8 shows an SEM micrograph of the cross-section of the sample described in Example 13.

**WE CLAIM:**

1. A breathable, waterproof, flexible, seamless shaped article which is comprised of a flexible layered composite comprising:
  - (a) a microporous, elastomeric, thermoplastic polyester polyurethane or polyether polyurethane Layer I that is water vapor permeable; and
  - (b) a hydrophilic, continuous nonporous polymer Layer II that is waterproof but water vapor permeable.
2. A breathable, waterproof, flexible, seamless shaped article which is comprised of a flexible layered composite comprising:
  - (a) a microporous, elastomeric, thermoplastic polyester polyurethane or polyether polyurethane Layer I that is water vapor permeable;
  - (b) a hydrophilic, continuous nonporous Layer II that is waterproof but water vapor permeable; and
  - (c) at least one fabric layer.
3. The shaped article of Claim 1 or 2 wherein the polyurethane of Layer I is the reaction product of a linear hydroxyl terminated polyester or polyether polyol and a diisocyanate and a low molecular weight diol.
4. The shaped article of Claim 1 or 2 wherein the hydrophilic polymer is capable of absorbing liquid water in amounts of at least 5% of its own weight when tested according to ASTM D570.
5. The shaped article of Claim 1 or 2 wherein the hydrophilic polymer is selected from an elastomeric copolyetherester, an elastomeric polyurethane or an elastomeric copolyetheresteramide.
6. The shaped article of Claim 1 or 2 in the form of a glove, mitten, sock or stocking.
7. The shaped article of Claim 3 in the form of a glove, mitten, sock or stocking.
8. The shaped article of Claim 4 in the form of a glove, mitten, sock or stocking.
9. The shaped article of Claim 5 in the form of a glove, mitten, sock or stocking.
10. A process for preparing a shaped article of Claim 1 which comprises dipping a nonporous shape former into a solution of a hydrophilic polymer, drying it to form a dry film of the

5 hydrophilic polymer on the former, then dipping the coated former into a solution of a thermoplastic polyether or polyester polyurethane, then immersing the former into a bath containing a liquid or liquid mixture which is a non-solvent for the thermoplastic polyether or polyester polyurethane, then drying the coated former and finally stripping the shaped article from the former.

10 11. A process for preparing a shaped article of Claim 2 which comprises treating a shaped fabric preform to make it water repellent and then mounting the treated preform on a nonporous similarly shaped former, dipping the former into a solution of a hydrophilic polymer, drying it to form a dry film of the hydrophilic polymer, then dipping the coated former into a solution of a thermoplastic polyether or polyester

15 polyurethane, then immersing the former into a bath containing a liquid or liquid mixture which is a non-solvent for the thermoplastic polyether or polyester polyurethane, then drying the coated former and finally stripping the shaped article from the former.

20

FIG. 1

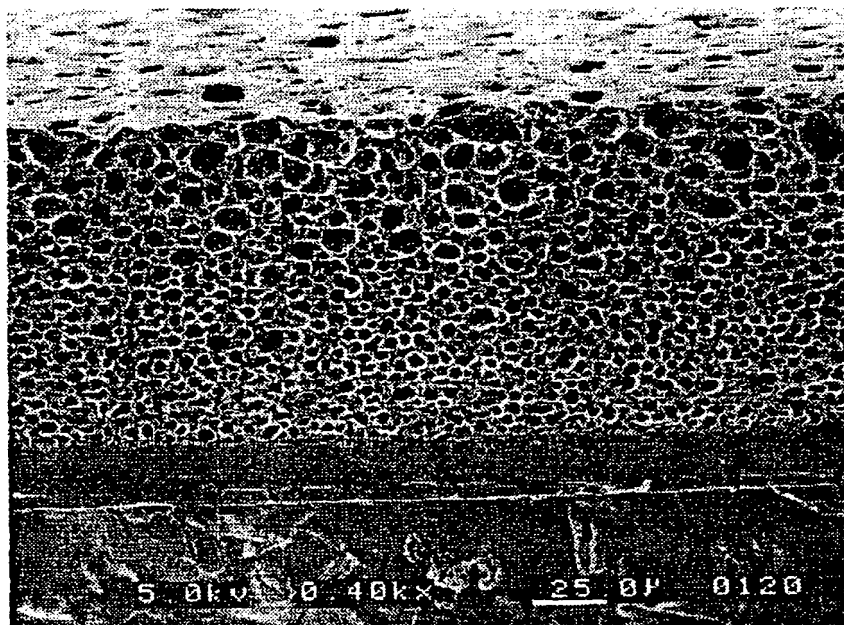


FIG. 2

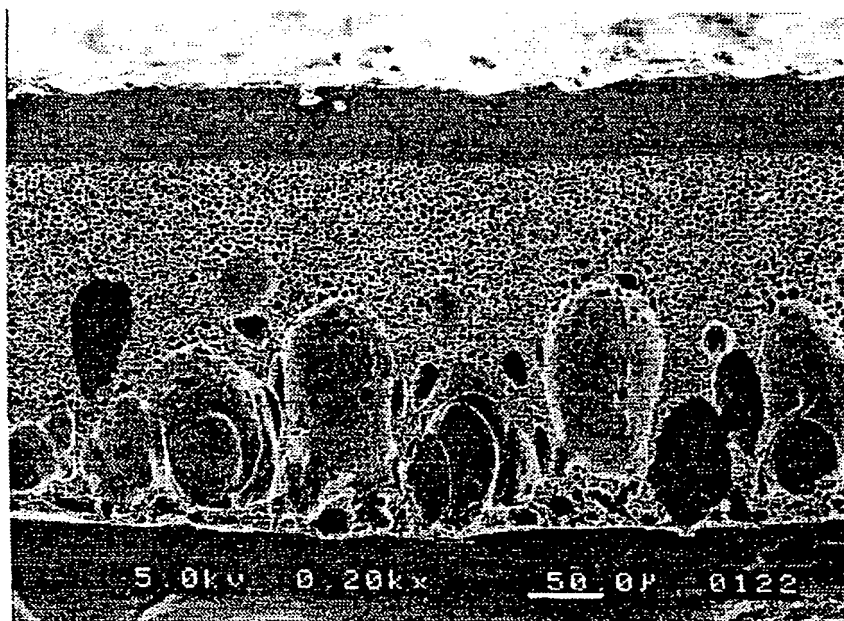




FIG. 3

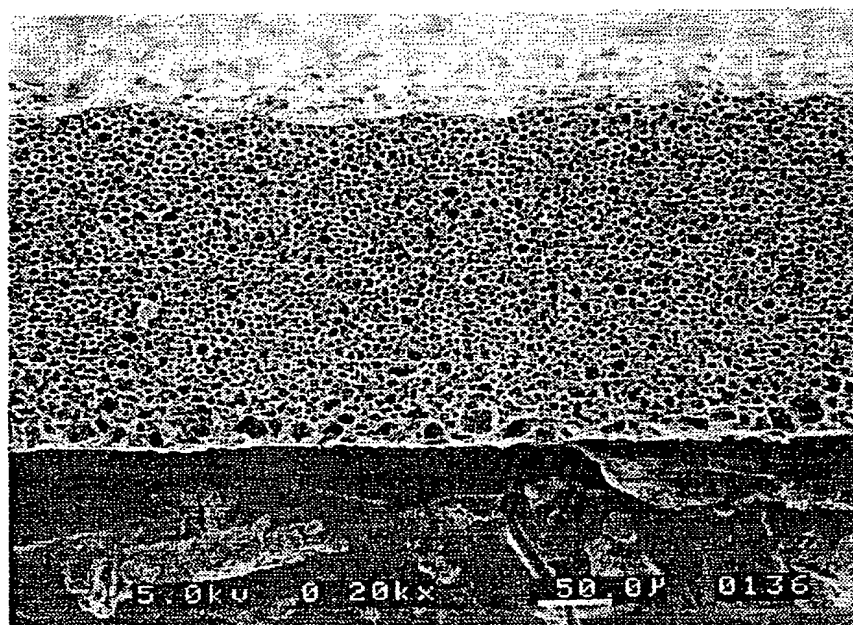


FIG. 4

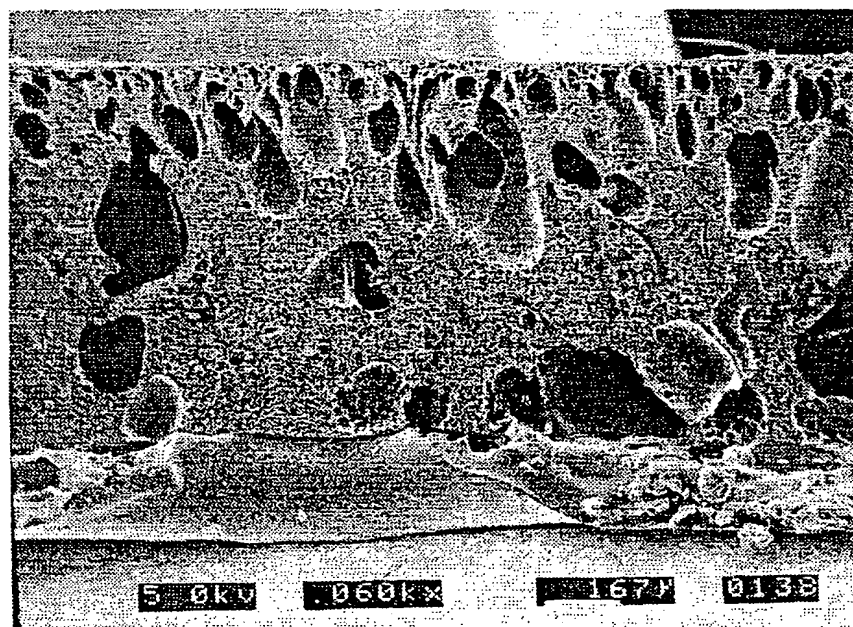


FIG. 5

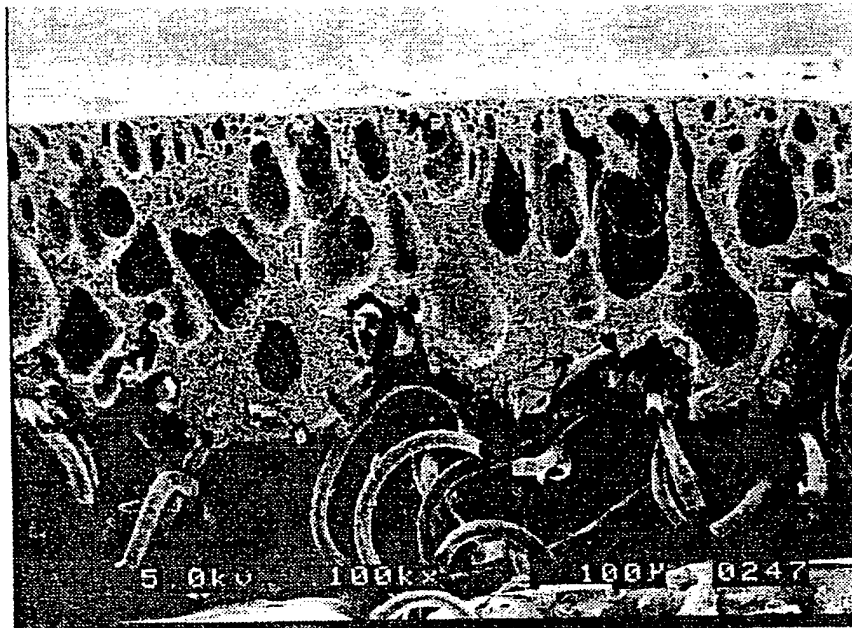
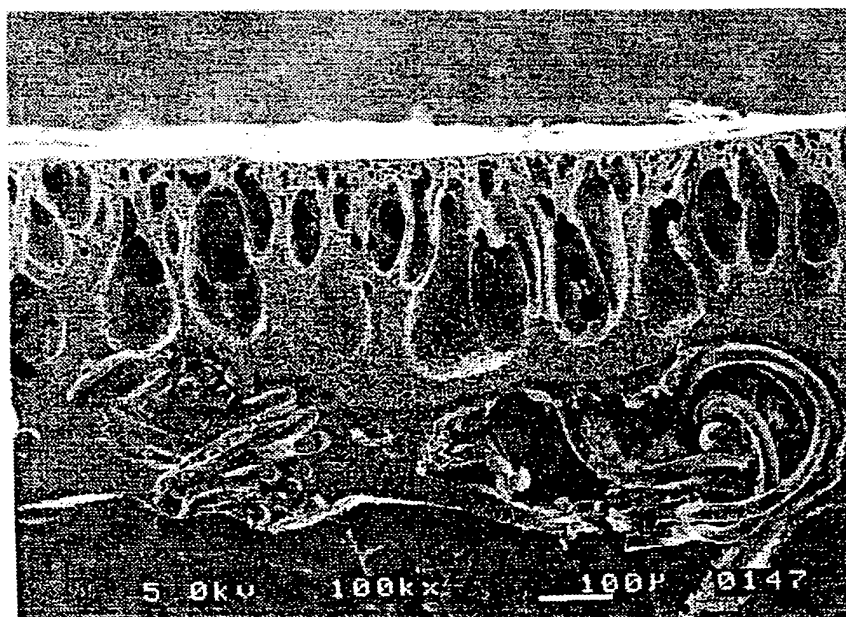


FIG. 6



Internal Application No  
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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 D06N3/14 B29C41/00 B29C41/14 B29C41/22 D06N3/18

**B. FIELDS SEARCHED**

IPC 6 B29C A43B D06N B29H A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI  Section Ch, Week 9415, April 1994  Derwent Publications Ltd., London, GB;  Class A05, AN 94-124453[15]  &amp; JP,A,06 073 669 (SEIKO KASEI KK) 15  March 1994  see abstract</p> <p style="text-align: center;">---</p>	1,2
X	<p>US,A,3 694 301 (L.E. GRUENEWALD ET AL.) 26  September 1972  see claims 11,12; example 4</p> <p style="text-align: center;">---</p>	1-5
Y	<p>EP,A,0 106 440 (SMITH &amp; NEPHEW ASSOC CO  PLC) 25 April 1984  see page 9, line 1 - page 12, line 12;  claims</p> <p style="text-align: center;">---</p>	1-11
	<p>---</p> <p>--/--</p>	

**Y** Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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**Date of the actual completion of the international search**

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FIG. 7

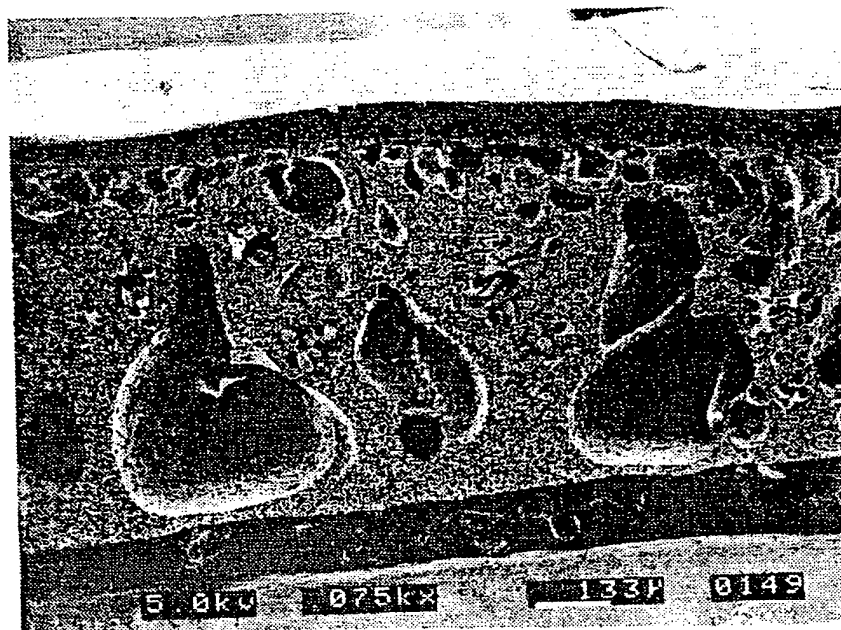
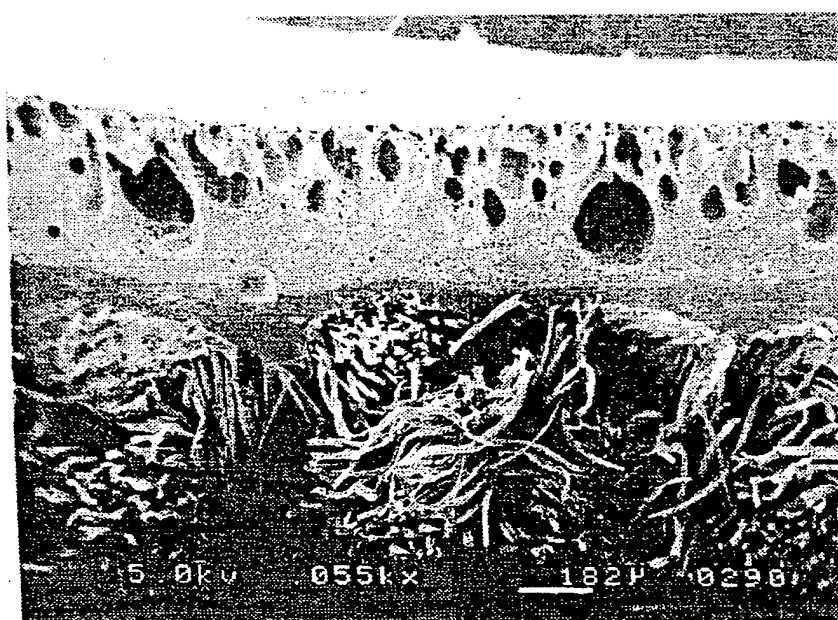


FIG. 8



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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB,A,2 181 691 (PORVAIR LTD) 29 April 1987 see page 4, line 30 - line 65; claims & US,A,4 888 829 cited in the application ---	1-11
Y	GB,A,2 024 100 (W.L. GORE & ASSOCIATES INC.) 9 January 1980 & US,A,4 194 041 cited in the application ---	1-5
Y	US,A,5 204 156 (LUMB ET AL.) 20 April 1993 see column 3, line 21 - column 4, line 6; claims 17,28,30,33 ---	1-5
X	WO,A,90 00643 (W.L. GORE & ASSOCIATES, INC.) 25 January 1990 see claims 1,20,24,35; figures 1,2 ---	1,2,4-10
Y	EP,A,0 310 037 (KURARAY CO., LTD) 5 April 1989 ---	1-11
Y	EP,A,0 398 611 (SLUMBERLAND HOLDINGS LIMITED) 22 November 1990 ---	1-11
Y	US,A,4 443 511 (WORDEN ET AL.) 17 April 1984 ---	1,2
Y	US,A,4 632 860 (D'ANTONIO ET AL.) 30 December 1986 see column 3, line 18 - column 4, line 25; claims 1,7 ---	1,2
A	US,A,3 501 326 (J. HOCHBERG ET AL.) 17 March 1970 -----	1-5

## INTERNATIONAL SEARCH REPORT

information on patent family members

Intern. Application No

PCT/US 94/07168

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3694301	26-09-72	NONE	
EP-A-0106440	25-04-84	AU-B- 563035	25-06-87
		AU-A- 1784283	16-02-84
		CA-A- 1209003	05-08-86
		DE-A- 3374656	07-01-88
		JP-C- 1759861	20-05-93
		JP-B- 4042021	10-07-92
		JP-A- 59049769	22-03-84
		US-A- 4995382	26-02-91
		US-A- 4672956	16-06-87
GB-A-2181691	29-04-87	US-A- 4888829	26-12-89
US-A-4888829	26-12-89	GB-A- 2181691	29-04-87
GB-A-2024100	09-01-80	US-A- 4194041	18-03-80
		CA-A- 1112551	17-11-81
		DE-A, C 2925318	17-01-80
		DE-C- 2954263	06-03-86
		FR-A, B 2429666	25-01-80
		JP-C- 1388850	14-07-87
		JP-A- 55007483	19-01-80
		JP-B- 60039014	04-09-85
		NL-A- 7904783	03-01-80
		SE-B- 445815	21-07-86
		SE-A- 7902163	30-12-79
US-A-4194041	18-03-80	CA-A- 1112551	17-11-81
		DE-A, C 2925318	17-01-80
		DE-C- 2954263	06-03-86
		FR-A, B 2429666	25-01-80
		GB-A, B 2024100	09-01-80
		JP-C- 1388850	14-07-87
		JP-A- 55007483	19-01-80
		JP-B- 60039014	04-09-85
		NL-A- 7904783	03-01-80
		SE-B- 445815	21-07-86
		SE-A- 7902163	30-12-79

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern al Application No

PCT/US 94/07168

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5204156	20-04-93	US-A- 5126182	30-06-92
		CA-A- 2068945	12-05-93
		EP-A- 0541206	12-05-93
		JP-A- 5239705	17-09-93
		US-A- 5268212	07-12-93
		US-A- 5364678	15-11-94
		CA-A- 2019474	17-04-91
		EP-A- 0445394	11-09-91
		JP-A- 3220377	27-09-91
WO-A-9000643	25-01-90	US-A- 4961985	09-10-90
		AU-B- 618112	12-12-91
		AU-A- 3872989	05-02-90
		DE-D- 68912545	03-03-94
		DE-T- 68912545	05-05-94
		EP-A- 0374245	27-06-90
		JP-B- 6067604	31-08-94
		JP-T- 2503335	11-10-90
EP-A-0310037	05-04-89	JP-A- 1085379	30-03-89
		JP-A- 1085377	30-03-89
		JP-B- 6037750	18-05-94
		DE-A- 3882319	19-08-93
		DE-T- 3882319	17-02-94
		US-A- 5156900	20-10-92
EP-A-0398611	22-11-90	AU-A- 5564590	18-12-90
		CN-A- 1048073	26-12-90
		WO-A- 9014461	29-11-90
		GB-A- 2232905	02-01-91
US-A-4443511	17-04-84	AU-B- 565226	10-09-87
		AU-A- 2192983	13-09-84
		CA-A- 1198045	17-12-85
		EP-A,B 0110626	13-06-84
		GB-A,B 2130525	06-06-84
		JP-C- 1719858	14-12-92
		JP-B- 4003741	24-01-92
		JP-A- 59187845	25-10-84

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 94/07168

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4632860	30-12-86	NONE	
US-A-3501326	17-03-70	BE-A- 687279	23-03-67
		DE-A- 1635592	03-02-72
		FR-A- 1494469	
		GB-A- 1122106	
		NL-A- 6613502	28-03-67



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